

WHAT IS CLAIMED IS:

1. A process for the enhancement of a metal catalyst for the catalytic hydrogenation of carbon monoxide, said catalyst comprising one or more members selected from the group consisting of Co, Ni, Cu, Ru, Rh, Pd, Os, Ir, Re and Pt, the process comprising:
- a) contacting with a hydrogen-containing gas at elevated temperatures so that at least a portion of the catalyst is in the metallic state;
  - b) impregnating under a non-oxidative atmosphere with a solution of a salt of at least one metal selected from the group consisting of Co, Ni, Cu, Ru, Rh, Pd, Os, Ir, Re, Pt, Mo, W, Si, Cr, Ti, Mg, Mn, Zr, Hf, Al, Th, La, Ce and Y, optionally in combination with at least one member selected from a group consisting of an ammonium salt, an alkyl ammonium salt, a weak organic acid and ammonia;
  - c) oxidizing with a gaseous oxidant in the presence of the impregnating solution; and
  - d) reducing with a hydrogen containing gas at elevated temperatures thereby forming an active catalyst.
2. A process in accordance with Claim 1, wherein said catalyst contains hydrocarbons and step a) additionally includes decreasing the hydrocarbon content thereof.
3. A process in accordance with Claim 2, wherein step a) additionally includes one of the following steps prior to contacting with a hydrogen-containing gas at elevated temperatures: treating with a solvent or supercritical fluid; contacting with an oxygen-containing gas or steam at elevated temperatures; and treating with a solvent or supercritical fluid, followed by contacting with an oxygen-containing gas or steam at elevated temperatures.

4. A process in accordance with Claim 1, wherein the impregnation solution in step b) contains a salt of a metal selected from the group consisting of cobalt, ruthenium, copper and nickel.

5. A process in accordance with Claim 1, wherein the metal salts in the impregnation solution in step b) are selected from the group consisting of nitrate, acetate, formate, citrate, carbonate and ammonium.

6. A process in accordance with Claim 1, wherein the impregnation solution in step b) contains a salt of the same metal as the catalyst metal.

7. A process in accordance with Claim 1, wherein said oxidant in step c) is selected from the group consisting of oxygen, air, ozone and nitrogen oxides.

8. A process in accordance with Claim 1, wherein the amount of said impregnating solution utilized in step c) is from about 10% to 5,000% of the calculated pore volume of the catalyst.

9. A process in accordance with Claim 1, wherein the temperature during the oxidation in step c) is maintained below about 100°C.

10. A process in accordance with Claim 1 additionally including the step of calcining under an oxidant-containing atmosphere after step c).

11. A process in accordance with Claim 1 additionally including the step of passivating after step d) by:

treatment with a carbon monoxide-containing gas under conditions such that the carbon monoxide is not significantly decomposed; or

treatment with a gas containing carbon monoxide and hydrogen under conditions such that the carbon monoxide is not significantly hydrogenated.

12. A process in accordance with Claim 1, wherein said catalyst  
5 comprises cobalt.

13. A process for the catalytic hydrogenation of carbon monoxide to produce a mixture of hydrocarbons in a carbon monoxide hydrogenation reactor utilizing a metal catalyst comprising one or more members selected from the group consisting of Co, Ni, Cu, Ru, Rh, Pd, Os, Ir, Re and Pt, said process  
10 including enhancing at least a portion of the catalyst during operation of said reactor by a process comprising:

- a) decreasing the hydrocarbon content;
- b) contacting with a hydrogen-containing gas at elevated temperatures so  
15 that at least a portion of the catalyst is in the metallic state;
- c) impregnating under a non-oxidative atmosphere with a solution of a salt of at least one metal selected from the group consisting of Co, Ni, Cu, Ru, Rh, Pd, Os, Ir, Re, Pt, Mo, W, Si, Cr, Ti, Mg, Mn, Zr, Hf, Al, Th, La, Ce and Y, optionally in combination with at least one member selected from a group  
20 consisting of an ammonium salt, an alkyl ammonium salt, a weak organic acid and ammonia;
- d) oxidizing with a gaseous oxidant in the presence of the impregnating solution; and
- e) reducing with a hydrogen containing gas at elevated temperatures  
25 thereby forming an active catalyst.

14. A process in accordance with Claim 13, additionally including the step of removing catalyst fines by

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i) classification or screening of a powder obtained in any step producing a powder; or

ii) decanting or classification of a catalyst slurry in any step producing a slurry.

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15. A process in accordance with Claim 13, wherein said catalyst is a supported catalyst.

10 16. A process in accordance with Claim 13, wherein said catalyst is a Dispersed Active Metal (DAM) catalyst.

17. A process in accordance with Claim 13, wherein said catalyst comprises cobalt.

15 18. A process according to Claim 13, wherein steps (a through (e are carried out in a single carbon monoxide hydrogenation reactor.

19. A process according to Claim 18, wherein the carbon monoxide hydrogenation reactor is a fixed bed reactor.

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20. A process according to Claim 13, additionally including the steps of withdrawing catalyst from a reactor and returning it to at least one reactor, wherein steps (a through (e are carried out subsequent to said withdrawing step.

25 21. A process according to Claim 20, where steps (a through (e are carried out prior to said returning step.

22. A process according to Claim 20, where steps (a through (e are carried out subsequent to said returning step.

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23. A process according to Claim 20, additionally including the steps of withdrawing catalyst from a reactor and returning it to at least one reactor, wherein at least one of steps (a through (e is carried out prior to said withdrawing step.

24. A process according to Claim 23, wherein at least one of steps (b through (e is carried out prior to said returning step.

25. A process according to Claim 13, additionally including the steps of withdrawing catalyst from a reactor and returning it to at least one reactor, wherein at least one of steps (a through (d is carried out prior to said withdrawing step, and at least one of steps (b through (e is carried out subsequent to said returning step.

26. A process according to Claim 25, wherein the catalyst is passivated after step a) and then withdrawn from the reactor.

27. A process according to Claim 20, wherein said reactors are slurry reactors and said catalyst is withdrawn as a mixture with hydrocarbons.

28. A process in accordance with Claim 27, wherein in step a) the catalyst particles are initially separated from the mixture.

29. A process in accordance with Claim 28, wherein the catalyst particles are initially separated from the mixture by filtration, or by gravitational or centrifugal separation followed by decanting the hydrocarbons from the catalyst particles.

30. A process in accordance with Claim 27, wherein the treated catalyst is returned to at least one slurry reactor by one or more of:

forming a slurry of the catalyst with liquid hydrocarbons and introducing said slurry into said reactor;

5 forming a suspension of the catalyst in a non-oxidizing gas and introducing said suspension into said reactor; and

transferring the catalyst to the reactor by gravity or pressure gradient.

31. A process in accordance with Claim 27, wherein said catalyst is  
10 withdrawn periodically during operation of at least one slurry reactor.

32. A process according to claim 27, wherein at least a portion of said catalyst is returned to at least one slurry reactor during operation thereof.

15 33. A process in accordance with Claim 27, wherein said catalyst is withdrawn continuously during operation of at least one slurry reactor.

34. A catalyst for the hydrogenation of carbon monoxide, comprising one or more members selected from the group consisting of Co, Ni, Cu, Ru, Rh, Pd,  
20 Os, Ir, Re and Pt, said catalyst being enhanced by the process of Claim 1.

35. A catalyst for the hydrogenation of carbon monoxide, comprising one or more members selected from the group consisting of Co, Ni, Cu, Ru, Rh, Pd, Os, Ir, Re and Pt, said catalyst being enhanced by the process of Claim 2.

25 36. A process for producing higher hydrocarbons by the hydrogenation of carbon monoxide by reaction with hydrogen at reaction conditions in the presence of an enhanced catalyst according to Claim 34.

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37. A process in accordance with Claim 36, wherein at least a portion of the hydrocarbons formed are upgraded to more valuable products by at least one of fractionation and conversion operations.

5           38. A process for producing higher hydrocarbons by the hydrogenation of carbon monoxide by reaction with hydrogen at reaction conditions in the presence of an enhanced catalyst according to Claim 34.

10           39. A process in accordance with Claim 38, wherein at least a portion of the hydrocarbons formed are upgraded to more valuable products by at least one of fractionation and conversion operations.

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